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POTENTIAL HAZARDS

IN

MOLTEN SALT BATHS

FOR

HEAT TREATMENT OF METALS

N.B.F.U. RESEARCH REPORT No. 2

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Committee on Fire Prevention & Engineering Standards
Research Division

1946

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FOREWORD

The fire insurance organizations have had a direct and vital interest in the hazards incidental to heat treatment of metals for many years. A newer process, involving the immersion of metal work in a molten mixture of a variety of chemical salts, particularly sodium and potassium nitrates, commonly referred to as the "Molten Salt Bath" treatment, has been drawn to the attention of the insurance field.

Wartime augmented uses of light metals for aircraft purposes, such as aluminum and low magnesium alloys, have greatly stimulated the development and adaptation of this heat-treating process. Though the use of the molten or fused salt as a metallurgical heating medium has resulted in the solution of many problems which troubled the metallurgist, it also created a new series of potential fire and explosion-hazard problems for the industrial inspector of the insurance engineering departments and the fire protection engineer.

It is to be recognized that while the molten salts are not themselves flammable, their operating temperature is such as to render them capable of instantly igniting any contacted combustible material. In addition, the nitrates are powerful oxidizing agents. In the highly heated state they become extremely active and, under a proper combination of circumstances, they will promote explosive reactions. It should be further emphasized that contact between the molten nitrate and cyanide salts or red-hot solid fuel will result in a reaction of explosive violence.

Accidents have occurred sporadically due to bad work habits and careless overheating of the nitrates. Serious bodily burns have resulted from spattering due to accidental contact with water. Injurious gassing and perforation of the bath container have resulted from thermit reactions between the wall metal and the article under treatment. In some instances, inadvertent dipping of magnesium castings have occurred, resulting in explosions which have been devastating in their effects, not only by wrecking furnaces and baths, but also by causing heavy fire and structural damages to factory buildings and tragic injury to personnel. Certain aluminum magnesium alloys may produce like explosions.

Considerable thought has been given by insurance associations and safety officials here and abroad to the general hazards of this problem. Those hazards which primarily concern the fire insurance groups are in the category of proper control and safe handling of this hot fluid material from a standpoint of fire prevention and fire protection. Investiga-

tions have been conducted by the National Board of Fire Underwriters in collaboration with interested salt bath and furnace manufacturers and principal industrial users, with the prime purpose of eliminating unsafe practices and reducing the sources of danger which may be encountered in the employment of these molten salts.

The present treatise represents a cooperative effort between the Research Division of the National Board and the engineering staff of the Factory Insurance Association to bring to light the contributory factors which have been responsible in a large measure for the majority of incidents encountered, and to suggest workable requirements and readily applicable regulations safeguarding nitrate heat-treating baths.

Although it is recognized that a number of serious accidents have occurred through neglect to observe certain elementary and rather obvious precautions, at the same time, this survey and study leads to the belief that salt baths can be made safe if the operating units are correctly designed and operated with reliable attention and exercise of proper supervision.

From all present indications, the commercial acceptance of the molten salt technique appears assured. It may be reasonably expected, therefore, that a greater number of such heat-treating installations will appear in increasing numbers in the immediate years ahead. Although the many advances in the art have been directed toward providing stronger, more durable and lighter engineering materials of construction, such a heating technique is expected to find valuable and very extensive application in other fields of industrial use. Reports already indicate the use of high temperature fluid-salts as efficient heat transfer mediums for chemical processing equipment (a new petroleum cracking process employs 1,000,000 lbs. of nitrate-nitrite mixture (HTS) per unit, and upwards of 25,000,000 lbs. is reported to be in circulation in this field). The latest and most interesting application is the use of these molten oxidizing salts as a time-saving cleansing agent for automobile tire molds in the rubber industry. Information reported herein should be of value to inspection authorities encountering these newer uses of molten sodium nitrate.

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SUMMARY

This publication concerns itself primarily with a thorough review of the fire and explosion hazards likely to be encountered through the use of molten salts as heating mediums in the heat treatment of various metals and alloys. Special emphasis is given to the more dangerous nitrate baths. Coverage includes the basic principles of metal conditioning and outlines the purposes, methods, and development trends within the industry. A brief review of the background of the heat treatment of metals is given, insofar as such knowledge is required to bring about a better understanding of the engineering problems related to this important process. A guiding comparison is focused on the following processes: furnace heating, induction heating, flame hardening, and finally molten baths.

The main topic of discussion is the molten salt bath process. This process is carefully analyzed from various viewpoints, such as theory of operation, salts employed, and their melting points, eutectic mixtures, low temperature baths, medium temperature baths, and high temperature baths. Attention is centered on the low temperature nitrate baths because they present the greatest potential hazard due to the chemical activity of the salt. The physical equipment of the operation is also discussed, including the salt bath containers which are fabricated from steel, corrosion resistant alloys, and ceramics. The analysis of the factors which affect the "pot life" or relative durability of the container are given due consideration. The procedures and heating devices used to bring the salt bath to the proper operating temperature are carefully scrutinized. Four principal heating methods are considered: oil-fired furnaces, gas-fired furnaces, immersed electrodes, and direct resistance electric heaters. The thermal and supplemental safety controls required to operate the bath efficiently and safely are described.

A number of typical salt bath incidents involving fires and explosions are summarized. These incidents indicate the attendant dangers of overheating of nitrate baths, accidental admixture of cyanides or inadvertent immersion of magnesium alloys in the nitrate bath, structural failure of the bath container, and improper remelting of a frozen bath. This is followed by a detailed discussion of the hazards of the process and the causes of the incidents are broken down for individual analysis and study. Some of the most important causes of fire and explosion in the process are as follows:

(1) Violent generation of steam due to water coming in contact with molten salt; introduced as "carry over" from a preliminary cleansing or quenching bath, overhead service piping, leaky roofs and condensation, operation of automatic sprinklers, and liquid foods placed on ledges near the baths for "warming-up" by workmen.

(2) Sudden and explosive expansion of air occluded in blow-holes of castings and that trapped in tubes, closed piping, or hollow metal work when immersed in molten baths without prewarming.

(3) Violent and uncontrollable chemical reactions between nitrate baths and carbonaceous materials such as oils, soot, graphite, and cyanide carry-over from adjacent carburizing baths.

(4) Vigorous and explosive reaction between overheated nitrate baths and aluminum alloys.

(5) Explosive reaction between normally heated nitrate baths and carelessly introduced magnesium alloys.

(6) Thermit-like reaction between aluminum alloy articles lost in bath and the iron oxide sludge blanketing and insulating the bottom of bath container.

(7) Structural failure of bath container while in operation under conditions tending to lower the normal durability. Reaction between metal of bath container and nitrate under localized overheating.

(8) Failure of temperature controls with consequent overheating of nitrate bath.

(9) Storage and handling of bulk supply of sodium nitrate, and careless disposal and storage of waste nitrate without regard to active properties of the salt.

(10) Accidental or uninstructed setting of temperature control above safe operating limits.

The final chapter recommends a series of precautionary measures and safeguards which will facilitate the safe operation of the process. Proper fire fighting instructions are included. An appendix with a glossary of the most common terms of the industry is also presented.

I. INTRODUCTION

This article will bring to the attention of the insurance group some of the facts concerning a process which has been in the "special hazard" classification for a considerable period of time. A discussion of the process and the methods of control will develop a better understanding of the safety problems which are involved and be of mutual benefit to all concerned. The leading "molten salt bath" manufacturers have been aware of the operational hazards of the process and a considerable amount of progress has been made towards the elimination of these difficulties.

The probability of fires and explosions in the low-temperature neutral baths is greater than in the medium or high-temperature process. This is due principally to the fact that the salts of the low temperature baths consist of varying compositions of nitrate and nitrite compounds. Such mixtures are powerful oxidizing agents and in the molten state they become very highly active, and, consequently, require greater care in handling. In addition to this fact, if allowed to reach a temperature above 1100° F. the nitrates attack the metal of the bath container, and at 1300° F. and above, the salts are subject to rapid breakdown, with emission of toxic and reactive fumes, the oxides of nitrogen. The principle hazards of the liquid salt bath process are:

(1) Fire by contact of molten salts with combustible materials.

(2) Explosion through chemical and physical reactions of hot nitrates with metal articles or bath container and accidental contact with water and carbonaceous materials, including thermit-like reactions.

(3) Physical danger to the operator.
   (a) Exposure to gassing from nitrous fumes.
   (b) Burns resulting on contact with molten salts through accidental splashes and spattering.

II. BACKGROUND OF HEAT TREATMENT

Heat treatment of metals has passed through numerous stages of development. The methods have progressed from the crude, slow operations of the village blacksmith shop to the present-day production-line treatment. The usual heat treatment process involves a progressive series of operations consisting of controlled heating and controlled cooling until certain desirable characteristics and improvement in properties are achieved. In recent years, the progress of the field has been accelerated by the war-time introduction of new

metals and alloys and operational technique. The present general trend of the industry is continuing towards uninterrupted production-line flow, and in certain mass production work there is being developed mechanized equipment which automatically steps through the entire cycle of treatment, from loading to unloading.

The heat treatment of metals results in any of the following effects:

(1) Changes in internal stress.
(2) Changes in the structural nature of the constituents from the effect of temperature.
(3) Changes in the surface composition of material as nitriding or carburizing.

At the present time four primary methods of heat treatment are practiced.

(1) Furnace heating.
(2) Induction hardening.
(3) Flame hardening.
(4) Molten bath heating.
    (a) Molten lead.
    (b) Molten salt.

Furnace heating is the application of heat to the metal surface by means of a heated, circulating, atmosphere and by radiation from furnace walls. The heat for this process is supplied by furnaces fired with oil, gas, coke, or coal. This is one of the most widely used methods of heat treatment.

Induction hardening consists of hardening of metal by heat treatment through high frequency electrical induction. The steel so hardened is usually heated above the critical range and then quenched with water sprays. This method is limited to special applications.

Flame hardening consists of the direct application of an oxy-acetylene flame to the work to raise the temperature of the metal. It finds application where the work is too large to enter the furnace or where the distortion must be minimized.

Molten bath heating consists of heating metals and alloys by immersion into a bath of molten lead or molten salt. These molten materials act as heat exchange mediums and exclude all contact of the work with the atmosphere. The baths are heated and maintained at proper temperature by means of such fuels as oil or gas or electricity. Recent reports indicate that approximately thirty per cent of all heat treatment is now accomplished by this method which represents a large increase in this direction within the past ten years.

III. BACKGROUND OF MOLTEN SALT METHOD

The heat treatment of metals by molten salt baths originated in England more than fifty years ago. It came into popular use in European countries as this method involved a low-cost installation and an accurate, reproducible method of heat treatment for various metals and alloys.

The "molten salt bath" treatment consists of the immersion of the metal work into a molten salt, heated to a desired temperature, for a specific period of time. The molten salt is contained in either pressed steel, welded steel, cast alloy, or ceramic pots, depending on operating temperatures to be maintained and the type of salts employed. These pots or bath containers were originally heated externally by coal, gas or oil-fired furnaces, or by electrical heating apparatus. This was later followed by the safer technique involving electrical resistance units placed directly into the bath material. Immersion of these resistance-heating devices is made possible through the protected covering of a seamless, non-corroding alloy sheath. The most recent and advanced development in internal heating is directed towards the electro-thermal principle with the use of immersed electrodes, utilizing the resistance of molten salt to passage of electricity. This arrangement avoids localized overheating because the heat is applied to the main body of the melt (heating through the bottom of the container is avoided) and the circulating convectional currents that are induced between the electrodes permit a uniform overall temperature to be controlled directly.

The sides of the container are well insulated against heat loss. It has been noted that about eighty-five per cent of the entire heat loss is through the top surface of the bath. A number of installations are designed with covers to guard against radiation loss and to conserve heat during the idling periods. Temperature controls are recommended to maintain efficient heat treatment and to develop a safe operational process. Modern large-bath equipment has recording pyrometers for this purpose and additional control devices, such as safety fuses (gold alloys) to guard against excessive temperature by shutting off the fuel supply or through "cut-out" of all electrical power.

The size of these baths range from the small individual pot furnaces to the large size mechanized units which can be built in accordance with the specifications of the job. (See Figs. 3 and 6). These specifications are determined by the purpose of the work and the physical limitations of the equipment such as weight, size, and special designs for production. The needs of the aircraft industry created the demand for the

immersed-electrode or internally heated baths of a capacity as high as 85,000 pounds, which are the largest in present-day use. These large units are capable of processing sheets and large structures up to 25 feet in length, a condition which presented difficulty in the adaptation of externally heated baths.

Theory

The principle or theory of the molten salt bath method for the heat treatment of metals is best described in the following definition of a molten salt bath: "A salt bath is technically termed as a melt or fusion composed of one or more relatively stable chemical salts which is designed to form a liquid-like and inert heating medium into which the metal work to be heat treated is immersed."

The outstanding characteristic of this method is the uniform and rapid rate of heat transfer from the molten salt bath to the metallic body. Claim is also made that much less equipment and a simpler degree of control is possible with salt baths than in the so-called gas-atmosphere-controlled heating furnaces. The rate of heat transfer is dependent upon the following variables:

(1) Size and shape of the work.
(2) Composition of work.
(3) Thermal conductivity of the work.
(4) Thermal conductivity of the salt bath.
(5) Temperature differential between the bath and the work.
(6) Viscosity of the salt bath.
(7) Velocity of motion of molten salt bath past the work.

Liquid salt baths are used primarily for heat treating operations such as carburizing, hardening, tempering, quenching, annealing and brazing steel, copper, and aluminum assemblies. The expanded use of lighter metals in the aircraft industry has brought the salt bath into the production-line operation, and emphasized the need for a heat treatment method which will accomodate the following factors:

(1) Temperature control within narrow limits.
(2) Rapid and uniform heating.
(3) Minimum of warping and distortion of work.
(4) Prevention of oxidation and scaling of work.

Various combinations and mixtures of salts are used in order to obtain desired effects. The melting point, specific heat, fluidity and "drag-out" losses and such chemical properties as thermal stability (working range) and corrosiveness,

along with the cost of the materials are the determining factors in the choice of a particular mixture. It is important that the salt mixtures which are used have these characteristics:

(1) Salts should be stable — retain composition without sludge formation.
(2) Salts should not fume corrosively.
(3) Salts should be removed from work easily.
(4) Salts should be noncorrosive to the work.
(5) Salts should have a low viscosity at operating temperatures.
(6) Salts should be non-hygroscopic.
(7) Salts should be nonoxidizing to work subsequent to heat treatment.

No one composition of the salt baths is typical. These mixtures differ widely in makeup and comprise hundreds of proprietary preparations, almost all are based on sodium and potassium nitrates, chlorides and carbonates. Various formulations have been developed with lower priced salts to reduce "drag-out" losses, inhibit both decomposition and volatilization, and render such baths more long-lived and economical.

The following tables list the various chemical salts that may enter into bath compounds and give simple formulations, indicating the various "melts" obtainable:

MELTING POINTS OF SALTS

Salt	Melting Point ° F.	Boiling Point ° F.
Barium chloride	1764	2840
Barium fluoride	2336	2552
Boric oxide (anhydride)	1071	2732
Calcium chloride	1422	2912
Calcium fluoride	2480	——
Calcium oxide	4662	5162
Lithium chloride	1135	2480
Lithium nitrate	491	——
Magnesium fluoride	2545	4069
Magnesium oxide	5072	6512
Potassium carbonate	1636	decomp.
Potassium chloride	1429	2732
Potassium cyanide	1174	——
Potassium fluoride	1616	2732
Potassium hydroxide	716	2400
Potassium nitrate	631	d. 752*
Potassium nitrite	567	d. 662*
Sodium carbonate	1564	decomp.
Sodium chloride	1479	2570
Sodium cyanide	1047	2714
Sodium fluoride	1796	3092
Sodium hydroxide	605	2534
Sodium metaborate	1771	2610
Sodium nitrate	586	716*
Sodium nitrite	520	608*
Sodium tetraborate	1366	2865
Strontium chloride	1603	——

*Mixtures of these salts result in higher boiling and decomposition temperatures than ordinarily encountered with the single salts (probably due to formation of more stable salt complexes).

MELTING POINTS OF SALT MIXTURES

All mixtures are eutectics* except those marked †
(Proportions given are percentage by weight.)

Mixture	Melting Point ° F.
Lithium nitrate 23.3, Potassium nitrate 60.4, Sodium nitrate 16.3	250
Potassium nitrate 53, Sodium nitrate 7, Sodium nitrite 40	285
Potassium nitrate 56, Sodium nitrite 44	295
†Potassium nitrate 51.3, Sodium nitrate 48.7	426
†Sodium nitrate 50, Sodium nitrite 50	430
Lithium chloride 45, Potassium chloride 55	666
Barium chloride 31, Calcium chloride 48, Sodium chloride 21	806
Calcium chloride 66.5, Potassium chloride 5.2, Sodium chloride 28.3	939
Calcium chloride 67, Sodium chloride 33	941
Barium chloride 48.1, Potassium chloride 30.7, Sodium chloride 21.2	1026
Sodium chloride 27, Strontium chloride 73	1049
†Potassium chloride 50, Sodium carbonate 50	1085
Barium chloride 35.7, Calcium chloride 50.7, Strontium chloride 13.6	1110
Barium chloride 50.3, Calcium chloride 49.7	1112
Potassium chloride 61, Potassium fluoride 39	1121
Sodium carbonate 56.3, Sodium chloride 43.7	1177
Calcium chloride 81, Potassium chloride 19	1184
Barium chloride 70.3, Sodium chloride 29.7	1209
†Potassium chloride 56, Sodium chloride 44	1220
Sodium chloride 72.6, Sodium fluoride 27.4	1247
Barium fluoride 70, Calcium fluoride 15, Magnesium fluoride 15	1454
Barium Chloride 83, Barium fluoride 17	1551
Calcium fluoride 48, Magnesium fluoride 52	1738

*Eutectic is that particular mixture of two or more substances which has a lower constant melting point than any other mixture of its constituents.

IV. DESCRIPTION OF PROCESS

Molten salt baths can be divided into three main groups or classifications which are segregated by virtue of useful temperature ranges.

(1) Low Temperature — (300° F. - 1000° F.) . .

The salts utilized in this operation are primarily nitrates and nitrites. During the war the shortage of potassium nitrate

induced the industry to use a 10-90 mixture of sodium nitrate and sodium nitrite. However, the usual mix is a 50-50 combination of sodium nitrate and potassium nitrate. From the standpoint of safety these salts present the principle hazard of the process.

The salts are usually maintained in a slightly acid condition, as basic salts will etch the work. Frequent laboratory analysis will indicate any change in the character of the bath. The maximum temperature recommended for the low-temperature bath is about 1000° F. Some writers indicate that gases, such as oxygen and nitrogen, are evolved from slowly decomposing salts at 700° F. Experience has shown that the salts will attack the container and the work at approximately 1100° F., and at temperatures above 1300° F., a breakdown reaction with other materials (possessing catalytic influences) occurs with evolution of gases, and in some instances toxic oxides-of-nitrogen have been formed.

Low-temperature baths have found a wide range of useful application. The greatly increased wartime production of aluminum alloys for the aviation industry has carried this specific method of heat treatment along with the tide. The attempt to apply this process to mass production work has developed continuous flow operations. Some of the most common heat treatment applications of the low-temperature salt baths are as follows:

(1) Heating of aluminum alloys.
(2) Blueing steels.
(3) Tempering steels.
(4) Quenching of carbon and low alloy steels.
(5) Martempering and austempering.

(2) Medium Temperature — (1000° F. - 1750° F.)

Medium temperature baths are usually eutectic mixtures consisting of chlorides and carbonates, and cyanides. The cyanides function as a preventive to the formation of a soft skin on certain low carbon steel work and they also facilitate the cleaning of the work. In addition cyanide-containing baths are used for case hardening or carburizing low carbon steels. The chlorides and other mixtures are used in the direct heat treatment of certain steels. In order to prevent a change in the chemical structure of the bath additional salts or "rectifiers" are added. The most common rectifiers are: boric acid, fused borax, or boric oxide. These baths do not present the same hazards as the low-temperature baths, but the use of cyanides call for special operational safeguards, as the cyanides are extremely toxic and emit toxic fumes when

brought in contact with acid mediums. They also will combine with nitrates with explosive violence in the molten state. The most common uses of the medium temperature salt baths are as follows:

(1) Normalizing, annealing, and hardening of certain carbon and alloy steels.
(2) Quenching and tempering.
(3) Annealing of non-ferrous metals.
(4) Preheating of high speed steels.
(5) Carburizing.
(6) Cyaniding.
(7) Brazing.

(3) High Temperature — 1750° F. - 2400° F.)

High temperature baths are not eutectics and sometimes they are referred to as "glasses". They are more limited in varieties of useful application than either of the other two classes of salt baths. These salts consist of a number of mixtures of barium chloride, borax, sodium fluoride, silicates, and magnesia or lime. There is an increasing trend toward the use of water-soluble compounds, containing primarily anhydrous barium chloride plus small additions of sodium chloride. Rectifiers containing ferro-silicon are also utilized. These baths are not always inert to the steel when initially employed, but they become more efficient after use. This is an exacting operation and at the higher temperatures accurate control is most important for successful heat treatment. It is necessary to preheat the work before immersion into the high temperature baths and the low and medium salt bath operations are used for this purpose. The high temperature salts have a tendency to stick to the work and they are not all water soluble. This necessitates cleaning of work with specific solutions such as a ten per cent solution of boiling sodium cyanide, molten caustic soda, or other salt baths. The gradual discarding of the borate salts will eventually result in the elimination of these cleaning procedures. The high temperature baths find greatest use in the following heat treatment operations:

(1) Hardening of high speed steels.
(2) Heat treatment of certain high alloy steels.
(3) Copper brazing.

Salt Bath Containers:

One of the limiting factors in the efficient and safe operation of the "molten salt bath" process has been the choice of container which could be used. These containers are fabricated from steel alloys or ceramic materials.

The composition of the steel pots varies from cast iron and low carbon steels to more corrosion-resistant high chromium and nickel alloys. The steel pots used in low-temperature nitrate baths are subject to more corrosive fumes and chemicals than pots exposed to other salts. Laboratory investigations in Germany have indicated a distinct advantage in the use of special steel alloys which are more resistant than ordinary forms of low carbon steel. For this reason the welded or cast chrome-nickel containers are preferable. Reactions between the salt and pot often cause scaling which leads to the possibility of uneven and local overheating.

Ceramic containers are used only in conjunction with electrode furnaces. Ceramic pots are usually made of refractory materials consisting of silica, oxides and silicates of magnesium, calcium and aluminum. These pots are subject to decomposition in the presence of alkaline salts.

As this equipment is used under extreme conditions and at very high temperatures, the useful span has been brief and often indeterminate. Newer methods of operation and the use of immersion electrode heaters have extended the use of pots beyond what was normally considered possible. In recent publications authorities on the subject have recommended that externally heated alloy pots utilized in conjunction with nitrate baths should be taken out of service, emptied, thoroughly cleaned and carefully examined at least once every six months. The pot life of a salt bath may vary from less than 300 hours to 4 years (ceramic pots have been known to exceed 5 years at temperatures below 2000° F.) and is dependent upon the following factors:

(1) Composition and quality of the container.
(2) Operating temperature of the salt bath.
(3) Method of operation.
(4) Nature of salt bath.
(5) Type of furnace or heating equipment.

Salt Bath Furnaces

The design and choice of a furnace is extremely important from the standpoint of safe operating conditions. It is essential that local overheating shall be avoided and, therefore, a flame should never be brought to impinge or bear directly upon the wall of the container. Coal fired furnaces are rarely used and are strongly advised against due to the lack of proper heat control and the most dangerous reaction of the molten nitrates with carbonaceous materials in the event of a pot failure. Gas and oil-fired installations should be properly adjusted so that soot formation is avoided. To preclude explosive (unburnt) gas and air mixtures in the event of flame

failure, a shut-off valve should be readily reached and quickly operated in an emergency. A safety pilot arranged to instantly close main gas valve in event of flame failure should also be provided. Leakage of stray currents in electrically heated units may lead to electrolytic corrosion and become contributory toward the perforation of the bath container wall.

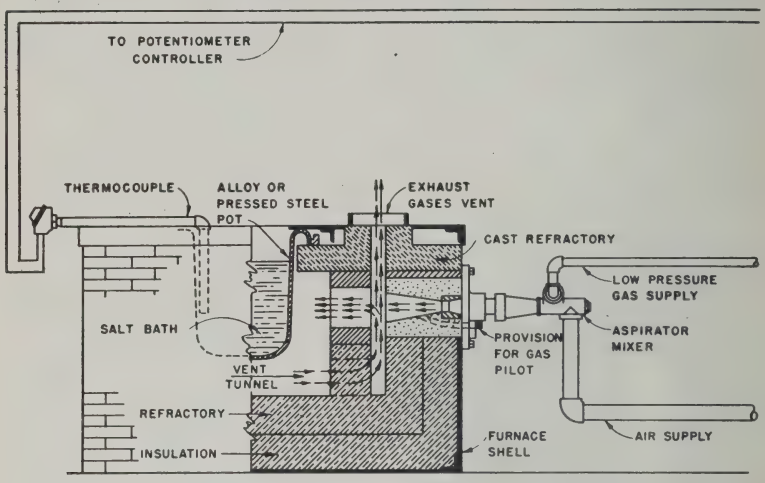

Fig. 1.—Fuel-fired Salt Bath—Gas Furnace Type

Four methods of heat application which have found general use throughout the industry are as follows:

(1) Oil-fired furnaces.
(2) Gas-fired furnaces.
(3) Electric resistance furnaces. (Immersed in bath or surrounding the pot.)
(4) Direct resistance electrode heaters.

The present trend is towards the use of the direct resistance electrode heaters, especially in larger installations, and it is reported that a large percentage of the molten salt bath equipment which is now marketed is furnished with this type of heating equipment. Some of the universally important points of salt bath furnace design are listed in the American Society for Metals—"Metals Handbook 1939".

Design of Furnace:

"(1) Apply heat as near the top of the pot as possible in order to obtain more uniform temperature and to start melting solid salt at the top. All molten salt baths are hotter near the bottom than at the top, because of the high

radiation losses from the surface. As all salt bath materials expand when heated, melting first near the bottom causes heavy pressures to be applied to the pot with the resultant deformation and early failure.

"(2) In fuel fired furnaces, the flame should not impinge upon the pot. Cylindrical pots with tangentially placed burners near the top, should be used whenever possible. The furnace should be vented near the bottom for the removal of flue gases. It sometimes pays to conduct the waste gases into an adjacent chamber where they may be used for preheating work.

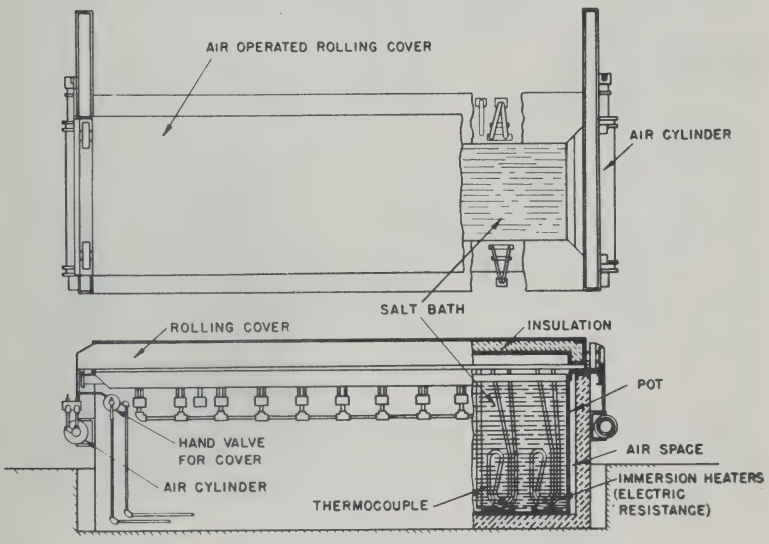

Fig. 2.—Electrically Heated Salt Bath—Resistance Heater Type

"(3) Bath materials and the fumes therefrom should be kept out of the combustion or heating chamber as refractories and heating elements are readily attacked by salts.

"(4) Combustion chamber atmosphere is important in relation to pot life. With steel pots in fuel fired furnaces a slightly reducing or soft flame is desirable. All openings should be plugged when the furnace is shut down to prevent circulation of air which would scale the hot container.

"(5) Furnaces should be of sufficient capacity to prevent a large drop of bath temperature when work is immersed and to allow all work to be immersed without touching or nearly touching the sides of the pot.

"(6) To conserve heat, pots should be covered whenever possible.

"(7) If the work is to be totally immersed in a salt bath, wire mesh baskets may be used for small parts, and the larger work may be suspended on hooks or by means of soft iron wire. The wire should be well annealed and must be twisted lightly with pliers in order to insure against work being lost in the pot when the wires become hot and sag.

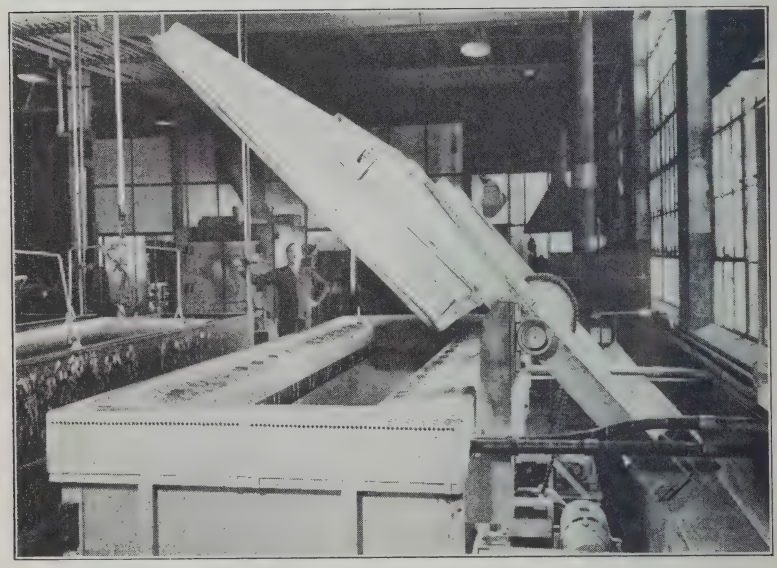

Fig. 3.—Large Salt Bath—Heated by Electric Resistance Immersion Units
(Loading Dimensions: 3 ft. wide x 4½ ft. deep x 15 ft. long)

"(8) A spare pot should be kept near every bath furnace. A small leak in a fuel fired furnace will quickly be detected as white "smoke" will come out of the flue gas vent. Time will usually be available for the molten bath material to be ladled into the new pot, after which the failed pot can be easily removed and the newly filled pot let down into the furnace, with little loss of time."

Thermal Controls:

Molten salt baths require accurate and reliable temperature controls to insure the proper operation of the process. An adequate number of thermocouples should be properly located

to catch all possible hot spots. It is desirable in most instances to have an additional control for safety purpose which automatically shuts off the heat when the temperature exceeds the operating range. The latter equipment may also be supplemented with an audible and visible alarm device to warn the operator of excessive temperature rise, thereby calling attention to any abnormal condition. This temperature measuring equipment is vital to the installation and it must be checked and calibrated at frequent intervals. The instruments utilized in this process of heat treatment are either thermometers, thermoelectric pyrometers, radiation pyrometers, or safety fuses which melt at specified temperatures. Mercury thermometers made of metal have been used with good results in the low-temperature nitrate baths, although the baths require additional safety controls. Pyrometers are universally used in the medium and high temperature baths. It is necessary to protect the instrument as much as possible from the corrosive effect of the molten salts. An additional portable pyrometer is recommended to regularly check all stationary equipment and to act as a movable safety control in the event of instrument failure.

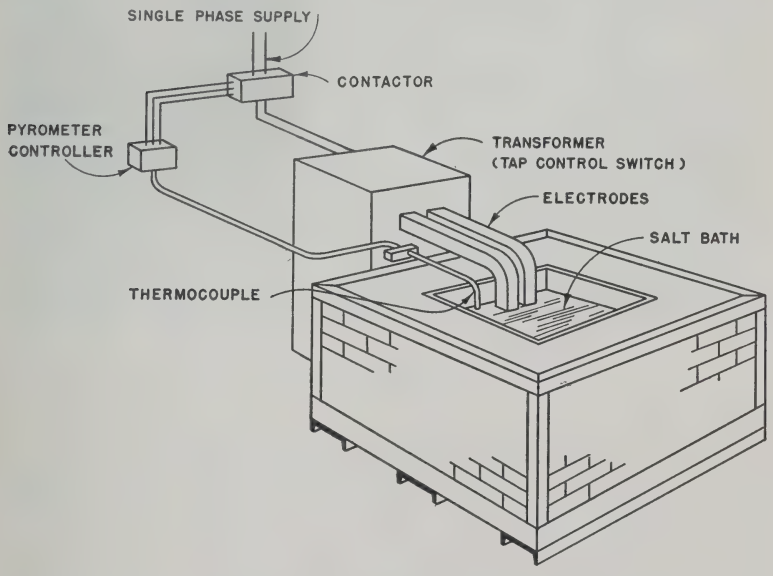

Fig. 4.—Electrically Heated Salt Bath—Electrode Immersion Type

Note: Safe practice utilizes a dual combination of thermocouples and electrical controls—see suggested recommendations (Section VIII—Precaution 10).

The use of a step-switch power transformer offers a simple and positive control for electrically heated salt baths. By this means the heating load may be easily reduced by setting at one of the lower voltage taps, when the bath is idling over long pauses of non-operating periods, or when left unattended at night and over week-ends. Danger from any faulty operation on the part of the thermostatic controls and relay circuits is circumvented through this added safety factor. This provision is extremely important as several incidents of failure have occurred during the prolonged idling periods.

Fig. 5.—Exploded Nitrate Bath Caused by Pot Failure
(Externally heated fuel-fired type)

V. MOLTEN SALT BATH INCIDENTS

The following set of incidents are typical and will serve as examples to indicate some of the points covered in the text to follow:

(1) A serious explosion and fire occurred recently in the heat treating division of a plant in a large western city. The explosion took place in a building housing a molten salt bath for heat treating aluminum alloy. The molten salts consisted of a (50-50) mixture of sodium nitrate and potassium nitrate.

This bath was heated by gas and during the night-idling period it was noted that the recording pyrometer registered a temperature of 1080° F. The night watchman attempted to reduce the flow of gas to the burners, but several hours later the bath was still overheated. It was then noted that the molten nitrates were foaming and running over the floor. Before proper action could be taken the bath exploded with such violence that one steel section weighing approximately 650 pounds was hurled a distance of 1,000 feet.

(2) An explosion and fire occurred recently in the heat treating department of a western manufacturer which took the lives of two employees and injured sixteen others. The bath consisted of the usual mixture of sodium and potassium nitrate which was normally operated at temperatures of 960° F. to 1,000° F. It was reported that the bath reached a temperature of 1300° F. to 1350° F. for a period of time directly preceding the explosion. The explosion was violent enough to cause a collapse of the structure which housed the heat treating department and caused fire in the oil quenching tanks. (The loss, including use and occupancy, exceeded $300,000).

(3) An explosion and fire occurred in a plant which was heat treating aluminum alloys. Magnesium alloy castings were accidentlly dipped into the nitrate bath which was heated to a temperature approximately 1000° F. An explosive reaction occurred and the plant and equipment were almost completely demolished.

(4) A steel bath container which held approximately 1700 pounds of a (50-50) mixture of sodium nitrate and potassium nitrate exploded during an idling period. The bath temperature was maintained by means of four gas burners and the flames impinged directly on the sides of the steel container. The apparatus was constructed by the user and did not adhere to the principles of good design. The temperature of the bath was recorded at 915° F. but a guard passing the bath noted that some of the exposed steel casing was heated to a red heat. Shortly thereafter the bath exploded. Pieces of steel were hurled through the roof and sides of the building and the molten nitrate was scattered about setting fire to pipe covering and other combustibles. From the condition of the steel container it was presumed by investigation that the welded seam of the vat was ruptured which allowed the molten nitrate to react violently with the accumulated carbon in the furnace.

(5) A small experimental molten nitrate bath, containing 500 pounds of a (50-50) mixture of sodium nitrate and potassium nitrate was involved in an incident, recently. This apparatus was heated by six automatically controlled gas burners

and was in the process of treating 35 pounds of aluminum castings at the time of the explosion. The last temperature noted by an employee was 980° F., but an examination of the bath and the aluminum casting indicated that the temperature must have been in excess of 1200° F. The building was of reinforced concrete construction and resisted the fire damage very well. The resulting explosion damaged the structure and would have resulted in a loss of life if the plant had been in operation at the time. Sections of the steel plate of the salt bath container were reduced from ½" to ⅛" by the rapid oxidation of the salts.

(6) Several years ago a fire and explosion occurred in Italy in the operation of a molten nitrate bath (damage caused amounted to 1,600,000 Italian lire — 40 carloads of refuse were removed). A metal container with a frozen salt bath was very rapidly heated from the outside, in such a manner that the salt melted first at the bottom. Pressure driving against the upper crust of salt ruptured the bath and drove the residual portion of salt through the roof of the building. The severity of the loss and explosion was explained by the fact that the nitrate reaction with the iron crucible resulted in the decomposition of the salt with the formation of gases.

(7) A nitrate bath used to heat-treat aluminum was the subject of an explosion in the metal working department of a large southern company. The bath was heated by an electrode immersion heater. The involved salts consisted of a 50-50 mixture of sodium nitrate and potassium nitrate. The pot was constructed of ⅜" steel, having dimensions 36" x 18" x 12". This bath was normally used at 920° F. to 950° F. and it idled at 500° F. However, due to a defect in the operation of the electrical equipment, the current was fed into the bath continuously and did not cut off when the temperature exceeded the operating range. The night watchman noted that the temperature rose to 1200° F. and that the liquid gave the appearance of boiling violently and throwing out small sparks. Directly thereafter, with the temperature rising rapidly, the explosion occurred, blowing the cover through the roof and causing a good deal of general destruction (loss exceeded $15,000).

(8) An explosion occurred in the heat treating department of a large eastern steel-alloy company. This explosion involved a large nitrate bath of the following dimensions, 16½' long, 16" wide and approximately 14" deep. The bath was gas-fired and was not in continuous operation. As the unit was restarted it was necessary to add additional salt and the temperature dropped to 420° F. Several hours later, when

the temperature was being elevated, a violent explosion occurred at 580° F. The damage was considerable and the loss exceeded $10,000. An analysis of the salt residue and investigation of the containers indicated that one can of cyanide had been mistakenly added with the nitrates to the nitrate bath. The combination of the salts caused the explosion as the temperature was increased.

(9) A fire occured in the heat treating division of a large metal-working plant, recently, which resulted in an explosion. The fire department was partly responsible for this explosion by carelessly deluging the heat treating section with streams of water. The water caused a tremendous steam explosion when it suddenly entered one of the molten salt baths. The steam pressure created was sufficient to destroy the structure and the loss was over $175,000.

VI. DISCUSSION OF HAZARDS

The hazards which are prevalent in the "molten salt bath" process may be divided into three main classifications:

(1) Fire by contact of molten salts with combustibles.
(2) Explosion through chemical and physical reactions.
(3) Physical danger to the operator.
    (a) Exposure to gassing.
    (b) Burns by molten salts.

The possibility of fire is present in all phases of the "molten salt bath" operations. The salts are worked at temperatures ranging from 300° F. to 2400° F. and contact of the heated salts with any combustible material will cause a fire. The sudden ejection, accidental spilling, popping or spattering of the hot salts has happened and produced the expected fire. The process, therefore, must be operated with attentive care and responsible supervision to avoid accidents. Housing the equipment in a noncombustible building and the removal of all combustible material from the area of operation are essential as a factor of safety.

Explosions have occurred in the operation of the molten nitrate baths. Nitrates will react with mild steel containers and start a brisk combustion process at temperatures as low as 1100° F., and this danger is particularly encountered from poor furnace conditions which contribute to local overheating. This is sometimes caused by accumulation of sludge or sediment in the bottoms of the pots where heating is applied externally through the bottom. Because of the possibility of this reaction with iron and steel, the nitrate bath should never be used above 1000° F. Aluminum alloys, with small amounts

of magnesium, are heated in the bath to temperatures approaching the critical melting points of the metals. It is possible for the molten nitrates to react explosively with such alloys when these critical temperatures are exceeded. Definite information is not available at present for fixing a safe maximum percentage of the magnesium. British observations report that firms regularly and safely heat-treat magnesium-aluminum alloys containing between 1 and 2 per cent magnesium in nitrate baths up to about 950° F., and with certain other special alloys of this type up to 1000° F., however evidence indicates that when higher temperatures are encountered a violent and explosive reaction may set in. The margin

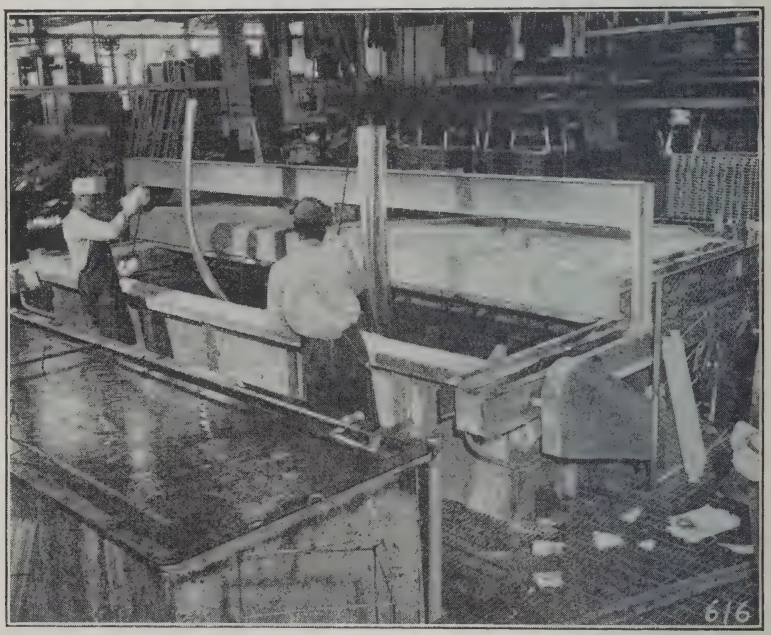

Fig. 6.—Large Nitrate Bath in Operation—Heat Treating Aluminum Airplane Sections.

Note: The following examples of good and faulty plant practice should be drawn to attention: Good Features—(1) Protective equipment on workers (face-shield, apron, asbestos gloves, and wire-fence guard around bath), (2) High ceilings for ventilation, (3) Motor-driven split cover over bath, (4) Solid handling hooks, (5) Fire-resistive and non-slipping metal floor-grating (removable for cleaning). Faulty Features—(1) Lack of segregation and overcrowded conditions, (2) Relative position (height) of quench bath to nitrate furnace, (3) Poor housekeeping—combustible litter on floor and exposed clothing suspended near operations.

of safety is narrow and the need for extreme care is obvious. According to the Aluminum Company of America authorities, magnesium alloys should never be heat-treated in nitrate under any circumstances, nor should aluminum alloys containing more than a few per cent of magnesium be treated in this similar manner.

The heated nitrates react strongly with all free or chemically combined carbonaceous material such as oil, soot, tar, cotton waste, graphite, cyanides, etc. Most of these materials will be found in the operating room by virtue of their use in some other integral part of metal heat treatment work. Accidental mixtures of cyanides with molten nitrates have caused explosions of considerable violence with tragic and serious losses. The accidental injection of a quantity of water into the molten bath may result in an instantaneous and explosive generation of steam, and cause a serious explosion or fire. Explosions have also occurred when air trapped in closed metal-work tubing (or occluded air in casting cavities and "blowholes"), undergoes rapid expansion in the molten salt bath.

Intensive external reheating and remelting of the solidified or frozen bath may result in rapid expansion sufficient to cause the bath to bulge and become dangerously strained, or enough pressure may be generated in the bottom to cause sudden breakage of the salt crust and dangerous scattering of the fused materials. To avoid such injurious overheating, starting coils and low voltage transformer taps have been employed, or vertical iron rods may be inserted before solidification to provide vent holes and prevent sealing of the gases underneath.

Safety provisions must be made for the operators of the molten salt bath process. The nature of the work indicates that most injuries to persons working on this process are caused by burns through molten salts. Protection to the clothing is essential, as ordinary garments will catch fire immediately when contacted. It is not advisable to allow clothing or work garments to become impregnated with nitrate salts, and, in addition, such contaminated articles should not be stored in the usual factory lockers with other personal belongings. The spatter of the extremely hot liquid salts on the body of the worker may result in dangerous or fatal burns.

British authorities indicate that good ventilation is essential to prevent accidental gassing by nitrous fumes. Other reports state that nitrates and nitrites may break down when undergoing chemical reaction with other materials, forming injurious gases. These oxides of nitrogen may be visible as reddish-brown fumes in high concentrations or they may be

obscured by smoke when present in low concentrations. The fumes are extremely dangerous and their insidious or delayed action eliminates the usual warning signal possessed by other more pungent and direct-acting gases, like chlorine or ammonia. It is, therefore, possible to inhale lethal quantities of this gas in the early stages of exposure without being aware of it. European practice requires that ventilating equipment should be installed over the bath, and gas masks should be available for emergency work.

Note: U. S. Dept. of Labor, Division of Labor Standards recommends a maximum safe concentration of nitrogen dioxide of 10 parts per million parts of air.

VII. CAUSES OF INCIDENTS

Steam Explosion and Spattering:

(1) Water in contact with the molten salt has caused explosions. The water may enter the bath in any one of the following ways:

(a) As a "carry-over" with work from nearby quenching tanks.

(b) Leaks of overhead water pipes or roof.

(c) Poorly designed ventilator systems which allow rain water or condensation (sweating of cold pipe and overhead steel structure on humid days) to drip into bath.

(d) Entrained moisture in compressed air used for agitating the liquid melt, or operating pneumatic control devices.

(e) Accidental spillage or splashes from nearby rinse tanks.

(f) From operation of opened sprinklers and foam systems or use of hose streams in fire-fighting.

(g) From food containers placed on the ledges or cover of the bath to heat the contents (coffee, tea, soup, etc.).

Resulting Hazards: Explosion - Fire - Burns.

Air Entrapment and Spattering:

(2) Air trapped in tubes or other metal work may expand with spattering of molten salt, or rupture the work with violent explosion when immersed into a molten salt bath.

Resulting Hazards: Explosion - Fire - Burns.

Reaction Explosions With Combustibles and Magnesium:

(3) Chemically free or combined carbonaceous material (cyanides - oil - grease - soot - graphite - dripping roof tar etc.) may accidentally enter the molten nitrates bath and explode with violent reaction.
Resulting Hazards: Explosion - Fire - Burns - Gassing.

(4) Explosive reaction between the molten nitrates and aluminum alloy metal work containing small amounts of magnesium. This is possible when the temperature of the molten salt exceeds 1000° F. It is for this reason that overheating should be guarded against.
Resulting Hazards: Explosion - Fire - Burns - Gassing.

(5) Bath container may fail structurally, releasing the contents of the molten nitrate bath into the furnace. This causes an abrupt and sudden overheating and possible breakdown of the salt when it contacts the hot firebrick and an explosive reaction with the soot, carbon and tarry accumulations in the furnace box.
Resulting Hazards: Explosion - Fire - Burns - Gassing.

Overheating of Salt and Destructive Thermit Reaction:

(6) Iron oxides may accumulate in the form of a sediment or sludge at the bottom of the molten nitrate bath; acting as a barrier against the heat introduced from the outside, a considerable store of stagnant heat may result and promote overheating of the wall metal and superheated, sudden and violent boiling, known as "bumping". The reaction of this sludge with any overheated aluminum alloy may cause a vigorous "thermit" reaction and explosion.
Resulting Hazards: Explosion - Fire - Burns - Gassing.

(7) Failure of temperature and heat controls (arcing and sticking of make-and-break electrical contacts of relay controls) may cause the overheating of the nitrate bath with consequent explosion. Disastrous accidents have occurred during over-night and week-end idling periods when the bath was not under direct observation or supervision.
Resulting Hazards: Explosion - Fire - Burns - Gassing.

(8) Localized overheating in nitrate baths may result in burning through the walls of the container, causing the dangerous contents to be released by slow leakage or sudden dumpage. In externally heated baths this would expose the escaped salt to the much higher temperature of the glowing firebrick of the furnace chamber; while in the internally heated units, the released melt through the cooler insulation

would have a tendency to freeze or solidify. This may be instigated by any of the following conditions:

(a) Poor circulation of molten salts.
(b) Defective and improperly located electric heaters.
(c) Faulty furnace construction or operation.
(d) Formation of excessive sludge on the bottom of the bath container, and greatly reducing heat transfer.
(e) Improper starting (heat regulation) and melting of the initially solidified or frozen nitrate bath.

Resulting Hazards: Explosion - Fire - Burns - Gassing.

(9) Accidental or uninstructed setting of temperatures of the bath above the safe operating limits by not fully informed or careless operators.

Resulting Hazards: Explosion - Fire - Burns - Gassing.

Improper Disposal of Waste Nitrates:

(10) Careless disposal of spent nitrates and unwanted residues without regard to the active properties of the salt.

Resulting Hazards: Explosion - Fire.

VIII. PRECAUTIONS RECOMMENDED IN THE OPERATION OF MOLTEN SALT BATHS

Building Construction and Location of Salt Bath

(1) The molten salt process shall be segregated in a room of two hours fire resistance provided for this purpose, and the immediate area should not be equipped with automatic sprinklers. The roof should be leakproof, and the amount of combustible material in the building should be kept to an absolute minimum. No wooden flooring, platforms, or benches should be permitted in the vicinity of baths.

(2) A liberal area, constituting the zone of operations, should be spaced-off immediately around the bath to avoid any congestion, and prevent interference with normal operations. Where the required speed of manipulation of the work to be treated necessitates close proximity of the quench bath, this secondary bath (water or oil) should be located at a lower elevation and be fitted with an appropriate deflecting baffle or guard to prevent any accidental splash-over into the molten salt bath.

(3) All water conveying devices (such as—overhead service pipes — sprinklers — flexible hoses — steam pipes, etc.)

should be placed in such a position that leakage into the molten salt bath is not possible.

(4) To disperse the heat and prevent the accumulation of deleterious fumes that might arise from some misuse or accidental overheating of nitrate-nitrite salts, baths and their furnaces which do not have hoods should be installed in the sections of the plant where the ceilings are at least twenty feet above the top of the furnace, and the ceilings provided with appropriate vents and other roof openings of standard fireproof construction. Where quarters are confined and congested, a sheet metal hood should be installed over any molten salt baths. The hood should extend beyond the edges of the unit, and the lower end of the vent stack should be screened off with a stout wire net to break the fall of any loosened deposits or accumulations that might occur.

Storage and Handling of Nitrate:

(5) Primary supply of nitrate salt should be stored away from heat and other reactive chemicals, in a separate, fireproof and damp-proof building. It should be kept locked at all times except when necessary to transport material in and out of it, and should be protected with a sign cautioning against fire. No secondary, loose storage in the heat treatment department should be permitted. The material should be added as fast as it is brought in and not allowed to be dumped on the floor for later addition.

(6) All salts should be carefully stored in tightly covered drums to prevent moisture pick-up (salts are slightly hygroscopic). Both drum and furnace should be prominently marked to make identification certain, thereby, preventing the accidental mixture of an explosive combination of salts. Precautionary measures should be observed to absolutely prevent the immersion of a magnesium alloy into a nitrate bath (which has been heated for aluminum alloy work).

Housekeeping and Waste Disposal:

(7) All combustible materials such as oil, cloth, paper, etc. which are used in other phases of metal processing should be removed from the immediate vicinity of the salt baths. Furnace chargings for "topping-up" or "make-up" additions should be made from metal containers; sacks and paper bags should be avoided.

(8) Waste nitrates and unwanted bath residues should be carefully discarded in water solution. By no means should this material be allowed to mix with other waste products to be burned in an incinerator.

Equipment, Controls and Maintenance:

(9) An approved device to prevent discharge of unburnt fuel should be installed in oil or gas-fired furnaces to serve as a safeguard in preventing the accumulation of an explosive gas or vapor mixture, in the event of furnace flame failure. Burners should be regularly inspected and adjusted to reduce soot formation to a minimum.

(10) Two independent, automatic, temperature control systems are advisable on all nitrate baths, one control for recording and another as an auxiliary and overriding "cut-out" to provide additional safety if the regular control fails. These controls should be carefully checked at frequent intervals. The thermal controls should be adapted to provide audible and visible warning and to prevent excessive temperature rise by direct check on the fuel and power flow into the heating units. Thermocouple protection tubes should be provided. These should be of seamless construction, and be thermally durable and corrosion-resisting. Added protection is also offered against thermocouple-breaks and broken connections through the use of automatic limiting controls, arranged with positive "shut-off" action, which inherently fails in the safe position. A greater number thermocouples may be required to effect more complete control in the large baths. These thermocouples should be located to catch all possible hot spots and arranged to indicate temperatures of the bath charge and container walls, particularly in the case of fuel-fired furnaces. Appearance of foaming, "boils", or excessive convection currents should be interpreted as an indication of dangerous "hot spots". All manual controls that might play an important role in an emergency should be located at a safe distance from the furnace. Warning of excessive temperature danger should be conspicuously placed at the temperature controls of the salt bath. A sturdy and durable sign for nitrate baths should state: "DO NOT PERMIT TEMPERATURES ABOVE 1000° F."

(11) The transformer step-switch should always be set down to the idling stop and the cover closed, when the molten salt bath is left unattended at the end of the work period.

(12) Heating nitrate baths with coal constitutes a hazardous practice and should be avoided. Externally fired (gas or oil) and electrically heated furnaces should be built to preclude the possibility of uneven or local overheating on the sides of the container. Direct flame impingement on the container should be avoided. Emergency storage in event of bath failure should be provided. This should include a low concrete ridge, or wall, around the bath at such a distance as to form, with the cement floor, a tank big enough to hold the contents of the damaged bath.

(13) Nitrate bath containers should be emptied and carefully inspected at least once every six months. When gas or oil furnaces are used, the sides should be examined for excessive scaling or pitting and other indication of weakness. The electrodes or heating units should be examined for possible deterioration. The life expectancy of this equipment is determined by a number of factors and the experience differs in various types of work. For externally-heated, fuel-fired furnaces, chrome-nickel containers are specifically recommended.

Operating Requirements:

(14) Any hooks or fixtures, ladles, etc., used in one bath should be thoroughly washed and perfectly dry before using in other baths. Avoid getting extraneous matter into the baths. In the case of chloride salt baths where the work or fixture has entrained oil it is not necessary to clean it, as the oil vaporizes and simply burns off at the surface of the bath without any serious consequences.

(15) To preclude the possibility of carrying over of water by wet work, all material drawn from quench tanks should be preheated to drive out moisture. All such quench tanks should be located far enough away and at such a level as to prevent accidental splashes of water from reaching the molten salt bath.

(16) Closed piping or other hollow metallic articles in which air is trapped shall not be inserted into a molten bath without making provisions for the venting of the thermally expanded air and exercising due care in gradual immersion. Tools of solid construction should be used, and tubular material avoided.

(17) Care must be taken not to leave any article in the bath after it is supposed to have been withdrawn. Sludge and small metal articles which have dropped to the bottom of the pot should be cleared from the bath at frequent intervals, depending upon the degree of operation. This should occur regularly at least every week or more often when the bath is in constant operation. The installation of a "catch all" type chrome-nickel wire basket near the bottom of the bath will greatly facilitate the recovery of small parts.

(18) Possibility of accidental immersion of magnesium alloys is ever present when these materials are processed in same areas with the aluminum work. Every effort must be made to prevent such occurrences by exercise of particular care in the complete separation of these easily confused alloys.

(19) If the operating temperature of the nitrate bath exceeds the maximum limit, the following emergency action should be taken:

1. Shut off the heat supply to the furnace.
2. Quickly remove all work from the bath.
3. Get all employees to safe location away from the bath.
4. Re-check bath temperatures and if it continues to increase after steps 1 and 2 have been taken, prepare for an explosion.
   a. Call Fire Department, briefly explain situation.
   b. Summon plant fire brigade for emergency standby.
   c. Open windows.

(20) A cold or "frozen" salt bath should be remelted or liquefied by applying the initial or starting heat as near to the top of the pot as possible. All solidified bath salts will expand when heated; and if heated in the usual manner in externally heated furnaces they will first melt near the bottom and cause formation of excessive pressures and effect deformation and possible failure of the pot. Localized overheating, sufficient to cause breakdown of the salts, may also result in gas production and pressures sufficient to burst and scatter the solid charge on top. Special devices, such as gas burners which heat the upper layer of the salt, or the use of a graphite link placed between the electrodes in the electrode-immersion type furnace, are recommended for this purpose by manufacturers.

Supervision and Instructions for the Operator:

(21) Workers in the immediate vicinity of the molten salt bath should be provided with proper safety equipment (face shields—asbestos gloves and asbestos aprons), and all clothes lockers should be constructed of metal or other incombustible material. Suitable gas masks should be provided for emergency use against oxides-of-nitrogen fumes. A 1 to 2 per cent boric acid solution should be available at all times to treat minor burns.

(22) The operation of the molten nitrate bath should be supervised by qualified personnel who are thoroughly familiar with the critical operating ranges and the attendant dangers in overheating the work.

(23) Suitable instructions shall be posted in a conspicuous location in the direct vicinity of the molten bath. The placard to be posted should contain all the essential information necessary to operate the molten bath and to maintain safe operating conditions. (See example: pages 34-35).

Fire Protection:

(24) An adequate supply of buckets of dry, clean sand should be provided at several points inside and outside of the room. Where large quantities of sand may be required, it should be handily stored in protected bins, equipped with shovels for application. Fires usually result from spillage and

leaks and are of a fast spreading nature and difficult to control. Sand is best used for slagging and diking purposes to confine and prevent the spread of the escaped melt. Carbon dioxide and approved dry powder type extinguishers may be used to extinguish burning carbonaceous material around the immediate vicinity of the salt bath. No vaporizing liquid (carbon tetrachloride), water, foam, or other aqueous extinguishing agents should be permitted in fighting molten salt fires. While it is obvious that the addition of water to a molten salt bath will in all probability cause formation of dangerous steam pockets and an explosion, precautionary warning notices "CHEMICAL BATH — USE NO WATER — EXPLOSION DANGER!" should be placed in prominent locations to prevent mistakes. All persons in the neighborhood of baths should be instructed as to the dangerous practice of using water and the correct use of the sand.

(25) Cautioning placard to warn firemen outside of factory of the presence of nitrate baths should be displayed at entrances of the plant. The management should invite the officers of the nearby fire companies to inspect and become thoroughly acquainted with the location of these baths.

An example of an operating instruction-placard issued by one of the large manufacturers is as follows:

OPERATING INSTRUCTIONS

Type **Nitrate Bath**

Serial No.....

1. Operating Temperature .....Maximum Temperature .....
2. For use on .....Volts.....Cycles .....Phase.
3. For use with .....salt.
4. Electrode spacing at salt line is.....inches, and at bottom is.....inches.
5. Normal (full load) operating current.....amps.
6. Normal (running) tap .....Volts.
7. Starting taps .....Volts.
8. Idling taps .....Volts.
9. Normal depth of salt.....inches. Electrode immersion .....inches.

OPERATING PRECAUTIONS FOR ELECTRIC SALT BATH FURNACE

1. DON'T put any work, that is not perfectly dry, into furnace bath.
2. DON'T allow work to touch the electrodes, sides or bottom of pot.
3. DON'T use CYANIDE SALTS in this furnace bath.
4. DON'T run the furnace continuously at temperatures higher than the maximum shown above.
6. DON'T add damp salt to the furnace bath.
7. DON'T run the furnace continuously on the starting taps.
8. DON'T allow work that falls off the fixtures, to remain in the furnace bath.
9. ALWAYS WEAR A FACE SHIELD, EXTENDING BELOW THE CHIN,

5. DON'T run the furnace at higher operating current than that shown above. If the ammeter reading is too high, check the following conditions in the order listed.
   A. Temperature control instrument set for excessive temperature.
   B. Transformer tap switch set on wrong tap.
   C. Thermocouple failure.
   D. Salt level too high.
   E. Electrodes too close together.
   F. Line voltage too high.
   G. Wrong kind of salt being used.
   H. Sludge accumulation touching bottom of electrodes.

AND ASBESTOS GLOVES WHEN LOADING OR UNLOADING THE FURNACE or WHEN ADDING SALT.

10. ALWAYS degrease work before putting it in the furnace bath.
11. ALWAYS keep cover closed as much as possible when restarting furnace.
12. ALWAYS keep the furnace and surroundings clean and free from salt drippings and any inflammable materials.
13. ALWAYS set transformer tap switch down to idling tap and close cover when furnace is to be left unattended at end of work period.

NOTE: Similar placards are issued with the medium and high temperature salt baths with the instructions that "salts used in one type of molten salt bath should not be used in another bath without considering the possibilities of reaction between the salts or bath container. Ceramic pots in particular are subject to fluxing and weakening when this occurs. The manufacturers' recommendation should be observed in this instance."

These placards generally include further detailed instructions which describe in step-wise detail the methods utilized in accomplishing the following operations:

(A) To shut down the furnace.
(B) To restart the furnace.
(C) Daily maintenance.
(D) Periodic maintenance.

It is suggested that responsibility for maintenance shall be assigned to some particular man or men to insure proper attention to such important details.

APPENDIX

IX. METALLURGICAL FUNDAMENTALS

The subject matter covered by this publication falls in the realm of metallurgy. A condensed introduction to the basic principles, along with a clarification of terms encountered herein, should serve to better understand the presented material.

Steels and other metal alloys are to be looked upon as solid solutions, whose internal structure is almost wholly dependent upon the exact relationship and state of combination of the components comprising the systems. Steels are known to be alloys of iron and carbon, and, in addition, they may contain other property-modifying elements, such as nickel, chromium, vanadium, molybdenum, etc.

Such physical properties as hardness, malleability and ductility are governed by the crystalline structure of the steel. Changes in the crystalline structure of alloys may be effected by a series of "heat treatment" processes. The crystalline structure assumes different forms at various temperatures, and numerous variations and rearrangements are possible depending upon heating and cooling, or quenching rates.

Carbon steels have definite critical points and critical ranges with respect to existence and changes in their microstructure. The exact temperature at which these points occur and the number of points depend upon the carbon content of the steel. Pure iron is allotropic ("many related forms") and may exist in four different states, namely, alpha, beta, gamma, and delta. Each of these is stable only between very definite temperature limits — alpha-iron up to 1415° F., beta-iron from 1400° F. to 1670° F., gamma-iron above the latter temperature to 2555° F., and delta-iron to just below the melting point, 2795° F. Thus transformation of one form to another occurs as several critical points are passed on cooling. The resulting characteristic crystalline structures are microscopically determinable.

Commonly encountered terms which describe types of heat treatment, include, annealing, normalizing, tempering, and hardening, and, in addition, there are such special treatments as carburizing, cyaniding, and nitriding. These terms are further defined in the following glossary:

Annealing: A heating-cooling process used to remove the stresses produced by cold working, to prevent cracking, and bring the alloy to a soft or workable state for machining. This is usually

accomplished by placing the pieces in a salt bath heating above the critical temperature and cooling in air or in a furnace or some hot medium (closed receptacle to exclude air and guard against scaling of the heated surface and oxidation of carbon) and holding in the predetermined range until uniformly heated, to produce the desired microstructure, and then followed by prolonged and slow cooling—as compared to unrestricted cooling in air.

Austempering: Controlled quenching of steel into a high enough temperature in which the formation of "martensite" is prevented by cooling in molten salt and then by air.

Blueing: (a) Producing an oxide film on steel blue in color (due to light interference), by low-temperature heating.

(b) Heat treatment of steel springs, to relieve cold working strains.

Carburizing: Process of increasing the carbon content of the surface of iron base alloys, by exposure, at a temperature below the melting point of the metal, to a rich source of carbon. This is done either in a liquid carburizing salt bath or by pack carburizing in such carbonaceous materials as bone, charred leather, wood charcoal, or coke are usually employed. When heated, they give off a gas containing carbon which diffuses into the steel surface, the degree of penetration depending upon temperature and contact time. Appropriate heat treatment will harden the surface, while the interior core remains in the original soft state.

Case Hardening: Production of a hardened surface on the steel by an operation which consists of carburizing a piece of steel, quenching either mildly or rapidly, reheating to refine the core, quenching rapidly, reheating again to refine and harden the case, quenching rapidly and finally tempering at a low temperature and cooling slowly. This process is now seldom used, and is rapidly becoming obsolete.

Cyaniding: Form of "case hardening" or surface hardening of steel obtained by heating it in contact with a molten cyanide salt (both to increase surface carbon and nitrogen), followed by quenching. Sodium or potassium cyanide salts, maintained at 1550 - 1600° F., are employed. The work is preheated to 750° F. and then immersed in the bath for 10 - 20 minutes.

Decarburizing: Removal of carbon from the outer surface of iron or steel, usually by heating in an oxidizing or reducing atmosphere. Water vapor, oxygen, and carbon dioxide are strong decarburizers. Reheating with adhering scale is also strongly decarburizing in action.

Hardening: A process for toughening steel by heat treatment. Usually requiring two operations (a) heating above the critical range, soaking at that temperature until mass is uniformly heated, and (b) quenching rapidly in brine, water, or oil, arresting transition from "austenite" to "pearlite" and resulting in the formation of "martensite" and some "troostite". This treatment produces a fine grained steel having a maximum "hardness" and tensile strength, minimum ductility and internal strain. In this condition the material is too hard and brittle for practical use.

Austenite: A solid solution of "cementite" in gamma-iron, produced when steel is heated above the critical range and only stable when maintained at a temperature above the critical range, and will attain perfect homogeneity if sufficient time is allowed. It decomposes normally into "cementite" and "ferrite" when the steel is slowly cooled below a certain temperature (not less than 1275° F.) but may be partly preserved down

to normal temperature by quenching, with a resulting increase in hardness of the steel.

Martensite: Main constituent of hardened steel — an intermediate form of "cementite" in "alpha-iron", obtained when the transition from "austenite" to "pearlite" is arrested. Martensite is the hardest structure obtained in steel.

Sorbite: A third intermediate form between "austenite" and "pearlite", appearing with "troostite" in tempered steels.

Troostite: Another intermediate form, similar to "martensite", which is often present in hardened steels. Troostite is generally present in drawn and tempered steels, whereas "martensite" is not.

Cementite: An iron carbide Fe_3C—the normal form in which carbon is present in steel. A very hard and brittle constitutent, producing a hardened quality in steels.

Eutectoid: An alloy or solution of two components which has the lowest fusing point. In every alloy there is one percentage combination of the two constituents that will fuse at the lowest temperature.

> **Note:** Lowest fusion temperature for upper critical point occurs at 0.85% carbon content (where greatest hardness from heat treatment is obtained). This alloy has been named the "eutectoid" steel. Steel with less than 0.85% C (composed of "pearlite" and excess "ferrite") is called "hypo-eutectoid" and with more than 0.85%, "hyper-eutectoid". Steels with excess ferrite are "hypo-eutectic" (practically all aircraft stock are of this type), and steels with excess cementite are "hyper-eutectoid" (tool steels). Alloy steels containing nickel, chromium, manganese, etc., possess similar critical points but they occur at different temperatures for each steel.

Ferrite: Pure "alpha-iron" in carbon steels—soft, very ductile, and virtually non-hardenable (tensile strength is about 40,000 lbs./sq. in.).

Pearlite: Normally a laminated structure (barely resolvable by finest microscope) consisting of alternate layers of "ferrite" and "cementite"—a mixture of six parts "ferrite" to one part "cementite" and resembling "mother-of-pearl" in appearance. This structure is relatively strong, hard, and ductile (tensile strength over 100,000 lbs./sq. in.). Occurs in steel as a result of transformation of "austenite" into an aggregation of "ferrite" and "cementite".

Martempering: Heat treatment of steel resulting in a "martensitic" structure with a minimum of residual hardening strains. The steel is quenched into a medium capable of extracting heat at a rapid rate and then transferred to a constant temperature both at a temperature just above that at which the "austenite" transfers into "martensite". When the piece has equalized in temperature it is removed and allowed to cool in air.

Nitriding: Surface hardening of special alloy steels by heating in contact with ammonia gas or other nitrogenous material. It is expected to eventually supersede "case hardening" by carburizing.

Normalizing: A form of annealing—to secure uniformity and destroy coarse structures, strains, etc., in metals, by heating to a temperature at which recrystallization takes place; specifically, in the case of steel, by heating above the upper critical point (about 100° F. higher) and then cooling fairly rapidly in still air, under controlled conditions. This is a rapid method of securing grain

refinement and machinability—the higher temperature (than in annealing) dissolves the "cementite" network surrounding each grain and brings all the metallic carbides into the "austenitic" form.
Quenching: In the heat treating of metals, the step of cooling metals rapidly in order to obtain desired properties is most commonly accomplished by immersing the metal in oil or water.
Tempering or Drawing: A process of relieving hardening strains or "annealing" in which the hardened metal is heated, a second time, to a temperature below the critical point and then cooled. With steel, tempering involves decomposition of "austenite" or "martensite", and precipitation of the carbides.

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